# Conductivity and microviscosity of electrolyte solutions containing polyethylene glycols

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Electrical conductivity of potassium chloride solutions containing polyethylene glycol (PEG) of different molecular mass was measured in a wide range of the polymer concentration up to 33 wt. % for PEG 300, 600, 2000, 4600, and 10 000. The data were used to find the dependence of microviscosity, $\eta_{micro}$, which characterizes the decrease of the ion mobility compared to that in the polymer-free solution, on the polymer volume fraction, $\phi$. We find that the dependence is well approximated by a simple relation $\eta_{micro}/\eta_0 = \exp[k\phi/(1-\phi)]$, where $\eta_0$ is viscosity of the polymer-free solution and $k$ is a fitting parameter. Parameter $k$ weakly depends on the polymer molecular mass growing from 2.5 for PEG 300 to its limiting value close to 2.9 for long chains. Using the $\phi$-dependence of microviscosity, we give a practical formula for the conductivity of PEG-containing electrolyte solutions. © *2003 American Institute of Physics.*
[DOI: 10.1063/1.1605096]

## I. INTRODUCTION

This paper deals with electrical conductivity of electrolyte solutions containing polyethylene glycol (PEG) of different molecular mass. We were motivated by recent experiments[1–7] in which PEG and other water-soluble polymers were used in studies of ion channels. The basic idea of these experiments is to learn about channels by measuring the variation of the channel conductance due to the addition of the polymer to the membrane-bathing solution. It is important that the effect of PEG of different molecular mass is qualitatively different. Long PEG molecules, that cannot enter the channel, change only access resistance of the channel.[2] Short PEG molecules easily enter the channel. This leads to a decrease in channel ionic conductance because the polymers partially block the channel. Measuring the PEG-induced conductance change, it is potentially possible to explore channel geometry.[6]

To analyze data on the polymer influence on the channel conductance, first it is necessary to measure polymer-induced variation of the electrolyte conductivity in the bulk solutions. Here we report such measurements for different PEGs in a

wide range of the polymer concentration. We find a simple formula that perfectly covers the data for PEGs with fixed molecular mass for the entire range of the concentration. The formula contains the only adjustable parameter, which varies with the polymer molecular mass only slightly. We believe that these results will be useful in future studies of ion channels.

Conductivity of PEG containing electrolyte solutions has been studied by several groups. The closest to the present study are those by Foster *et al.*[8] and Bordi *et al.*[9] The most interesting qualitative result found in these studies is that the polymer effect depends mainly on the amount of PEG added into the solution and very weakly on the PEG molecular mass. This means violation of Walden's rule.[10,11] This rule, written in the form convenient for the present study, provides a relation between conductivity, $\sigma$, and viscosity, $\eta$, of the solution,

$$\frac{\sigma\eta}{n_{KCl}} = \text{const}, \tag{1.1}$$

where $n_{KCl}$ is the electrolyte concentration. The rule is violated because the viscosity of polymer containing solutions strongly depends on the polymer molecular mass[12] while conductivity does not. The violation is demonstrated in Sec. II.

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The effect of adding a polymer on the solution conductivity has two aspects: (1) lowering of the electrolyte concentration by the factor $(1-\phi)$, where $\phi$ is the polymer volume fraction, and (2) decrease of the effective mobility of ions due to their "collisions" with the polymer molecules. It is convenient to discuss the polymer influence on the mobility in terms of microviscosity, $\eta_{\text{micro}}$, introduced by the relation,

$$\frac{\eta_{\text{micro}}}{\eta_0} = (1-\phi)\frac{\sigma_0}{\sigma}, \tag{1.2}$$

where $\sigma_0$ and $\eta_0$ are conductivity and viscosity of the polymer-free electrolyte solution.

Here we report on our study of electrical conductivity of 0.1 M KCl solutions that contained PEG of different molecular mass: 300, 600, 2000, 4600, and 10000. The PEG concentration varied from 0 to 33 wt. %. One of the main results of our study is a simple formula,

$$\frac{\eta_{\text{micro}}}{\eta_0} = \exp\left(k\frac{\phi}{1-\phi}\right), \tag{1.3}$$

where $k \cong 2.9$ for sufficiently long PEG and $k \cong 2.5$ for PEG-300. We found that the dependence in Eq. (1.3) works amazingly well for the entire range of the concentrations for each of the polymers. When the ratio $\eta_{\text{micro}}/\eta_0$ is known one can easily find the conductivity using the relation in Eq. (1.2).

The problem of the polymer effect on the ionic mobility is a special corner of a more general problem of the tracer mobility in a polymer-containing solution. The latter has been intensively studied over a broad range of the problem parameters, including variation in size and nature of the tracer as well as variation of the concentration and type of polymer. One can find a good set of references on the subject elsewhere.[13–15] One of the main objectives of those studies was to find the dependence of the diffusion coefficient of the tracer on its hydrodynamic radius, $R$, as well as the concentration and molecular mass of the polymer, $c$ and $M$, respectively.

For semidilute solutions Langevin and Rondelez[16] suggested (with the reference to de Gennes, Pincus, and Velasco's personal communication) that the ratio of the tracer diffusion coefficient, $D$, to its value in pure solvent, $D_0$, is given by

$$\frac{D}{D_0} = \exp\left[-\left(\frac{R}{\xi}\right)^{\delta}\right] + \frac{\eta_0}{\eta}, \tag{1.4}$$

where $\xi = \xi(c)$ is the correlation length, $\xi(c) \propto c^{-\nu}$, and $\delta$ and $\nu$ are scaling exponents. The relation in Eq. (1.4) leads to $D = D_0\eta_0/\eta$ for $R \gg \xi$. For not so big tracers this relation predicts larger values of the diffusion coefficient. This might be interpreted in terms of microviscosity, i.e., an effective viscosity felt by the tracer, which is smaller than the solution viscosity.

Another expression used in the literature for the ratio $D/D_0$ gives this ratio in the form[17,18]

$$\frac{D}{D_0} = \exp(-\alpha c^{\nu}), \tag{1.5}$$

where $\nu = 0.5-1$ [this $\nu$ should not be confused with the exponent in the Langevin–Rondelez expression for $\xi(c)$] and $\alpha$ is a function $R$ and $M$, which does not depend on the polymer concentration. Dependence of this type with $\nu = 1/2$ was derived by several authors.[19–22]

The dependencies mentioned above are applicable for not too small tracers. They are inapplicable for ions because their sizes are small compared with all characteristic length scales associated with the polymer and the polymer network. Lowering of the ion mobility in the presence of the polymer compared to its values in the pure solvent is caused by steric hindrances to ionic motion rather than more efficient dissipation. Variation of the tracer mobility induced by steric hindrances is often treated in terms of the effective medium theory originally introduced by Maxwell.[23–25] We briefly discuss applications of this approach to analyzing data on the PEG influence on the electrolyte mobility in Sec. IV.

Deviations from the relation, $D \propto \eta^{-1}$, applicable for big tracers, are not a privilege of polymer-containing solutions. Similar deviations have been found in other systems.[26–32] The deviations are sometimes described by the empirical relation, $D \propto \eta^{-\alpha}$, with $\alpha < 1$. For example, in Ref. 26 it was found that mobility of simple ions in aqueous sucrose solutions decreases with the solution viscosity as $\eta^{-0.7}$. The authors of Ref. 26 indicate that this fractional dependence on the viscosity was proposed much earlier, in 1908.[30] Another example is the diffusion of xenon in liquid alkanes studied in Refs. 31 and 32, where it was found that $D$ is proportional to $\eta$ to a power close to $(-2/3)$.

The outline of the present paper is as follows: Experimental results are presented in the following section. Simple formulas for microviscosity and conductivity are introduced in Sec. III and then discussed in Sec. IV.

## II. EXPERIMENTAL RESULTS

Polyethylene glycols of molecular weights of 300, 600, 2000, 4600, and 10000 Da were purchased from Aldrich (St. Louis, MO). A 0.1 M KCl stock solution was prepared by the addition of doubly distilled water to the salt. Polymers were added to the stock solution to concentration of 2, 5, 7, 9, 11, 13, 15, 18, 21, 24, 27, 30, and 33 wt. %. The complete dissolution was determined visually.

Conductivity measurements were made with a CDM 83 Conductivity meter (Radiometer, Copenhagen). A thermostated CDC 324 cell was used. All experiments were carried out at 23 °C±0.1 °C. The conductivity cell was rinsed with doubly distilled water and ethanol, and dried by vacuum suction between each measurement.

Raw conductivity data were corrected for the electrolytic impurities inherent to the PEG production process. To achieve this, we measured conductivities of PEG solutions in doubly distilled water without KCl. This conductivity was subtracted from the raw conductivity, and the corrected value was used for all subsequent computations. In all cases the correction was less than 1%.

Solution viscosity was measured using calibrated Cannon-Ubbelohde viscometers. Because a given viscometer can only accurately measure a limited range of viscosities,
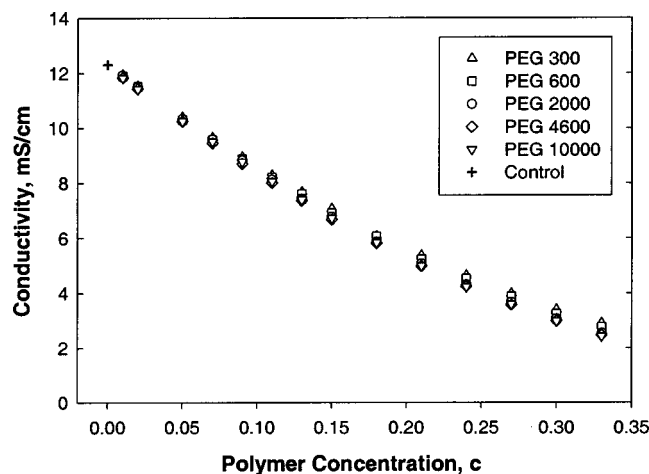
FIG. 1. Conductivity of 0.1 M KCl aqueous solutions containing differently sized PEG as a function of the PEG concentration (23.0 °C).



FIG. 3. Viscosity of the solution, $\eta$, divided by the viscosity of the polymer-free solution, $\eta_0$, as a function of the polymer volume fraction for polymers of different molecular mass.

three viscometer sizes (size 50, 100, and 200) were used to obtain the whole data set. The viscometers were placed in a constant temperature water bath, set at 23 °C±0.2 °C. Approximately 10 ml of each sample was used for a measurement. The solution was allowed to equilibrate to the set temperature for 20 min prior to the onset of the viscosity measurement.

Conductivity of PEG containing solutions is shown in Fig. 1 as a function of the polymer weight/weight concentration, $c$,

$$c = \frac{m_{PEG}}{m_{PEG} + m_{PFS}}, \tag{2.1}$$

where $m_{PEG}$ and $m_{PFS}$ are masses of the polymer and polymer-free electrolyte solution (PFS), respectively. Using these data one can find the ratio of the microviscosity to the viscosity of the polymer-free solution by Eq. (1.2) as a function of the polymer volume fraction $\phi$. This fraction is related to the polymer concentration by
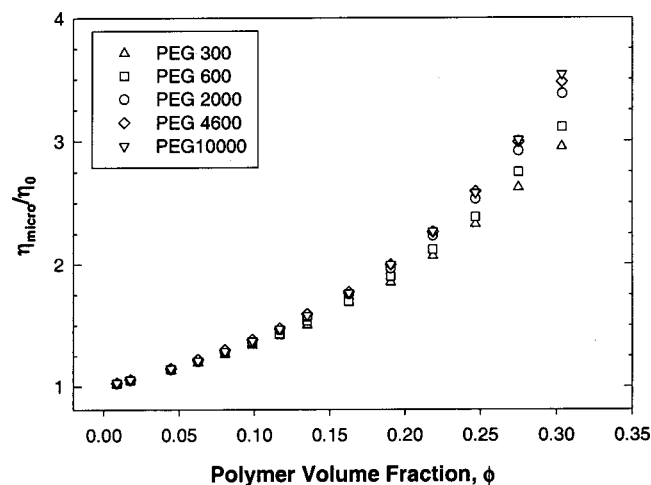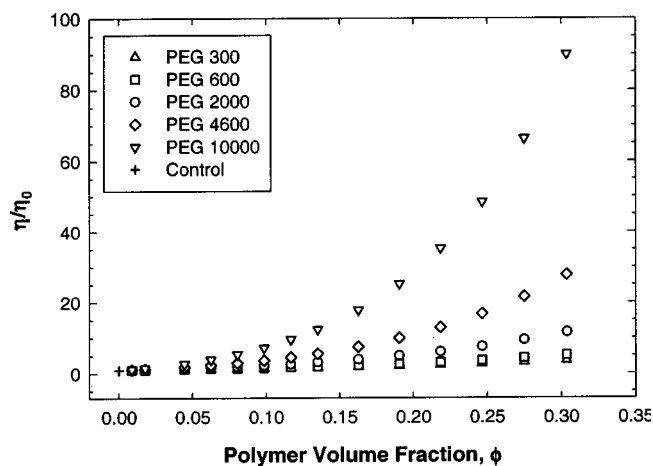
$$\phi = \frac{c}{c + \alpha(1-c)}, \tag{2.2}$$

where $\alpha = \bar{v}_{H_2O}/\bar{v}_{PEG} \cong 1.13$. For partial specific volumes of water and PEG we accepted $\bar{v}_{H_2O} = 1 \text{ cm}^3/\text{g}$ and $\bar{v}_{PEG} = 0.885 \text{ cm}^3/\text{g}$. The value of $\bar{v}_{PEG}$ is given in Ref. 9. The dependence of the ratio $\eta_{micro}/\eta_0$ on $\phi$ is shown in Fig. 2.

It is instructive to compare $\eta_{micro}/\eta_0$ with the ratio of the viscosity of the polymer containing solution to $\eta_0$ shown in Fig. 3. One can see that microviscosity depends mainly on the amount of PEG in the solution and only weakly depends on the PEG molecular mass. In contrast to microviscosity, viscosity of the solution is dramatically affected by the size of PEG molecules. Viscosity grows with the polymer volume fraction faster than microviscosity. The larger the polymer, the stronger this effect is pronounced. To illustrate this we give the ratio $\eta/\eta_{micro}$ in Fig. 4. The ratio at $\phi=0.3$ varies from ~1.2 for PEG 300 to ~25 for PEG 10000. Figure 4 clearly demonstrates Walden's rule violation since $\eta/\eta_{micro} = \sigma\eta/[(1-\phi)\sigma_0\eta_0]$ while according to Walden's rule it should be a constant.
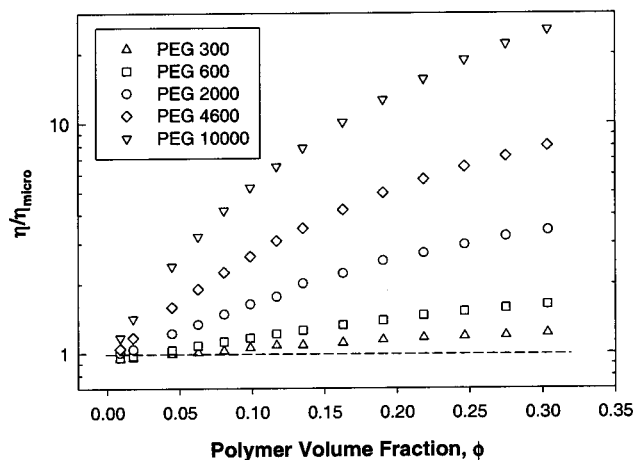


FIG. 2. Microviscosity, $\eta_{micro}$, divided by the viscosity of the polymer-free solution, $\eta_0$, as a function of the polymer volume fraction.



FIG. 4. Violation of Walden's rule.

TABLE I. Fitting parameters $k$ and $k'$ for PEG of different molecular mass.

| $M$ | 300 | 600 | 2000 | 4600 | 10000 |
|-----|-----|-----|------|------|-------|
| $k$ | 2.537 | 2.646 | 2.820 | 2.880 | 2.906 |
| $k'$ | 2.245 | 2.342 | 2.496 | 2.549 | 2.572 |

## III. FORMULAS FOR MICROVISCOSITY AND CONDUCTIVITY

When analyzing our data on $\eta_{\mathrm{micro}}/\eta_0$ we found that the ratio is very well approximated by the expression,

$$\frac{\eta_{\mathrm{micro}}}{\eta_0} = \exp\left( k\,\frac{\phi}{1-\phi} \right), \tag{3.1}$$

which contains the only fitting parameter $k$. Values of $k$ found from the data for each PEG are given in Table I.

Figure 5 demonstrates high quality of the approximation formula in Eq. (3.1). The numbers in Table I show that $k$ increases with the polymer molecular mass from $k \cong 2.5$ for PEG 300 and approaches a plateau value, $k \cong 2.9$, for long molecules. Variation of $k$ with molecular mass is shown in Fig. 6.

Using the relations in Eqs. (1.2) and (2.2) one can find approximate formula for the conductivity,

$$\frac{\sigma}{\sigma_0} = \frac{\alpha(1-c)}{c+\alpha(1-c)} \times \exp\left( -k'\,\frac{c}{1-c} \right), \quad k' = \frac{k}{\alpha}. \tag{3.2}$$

Values of $k'$ for PEG of different molecular mass are given in Table I. To illustrate high accuracy of this formula we calculated relative error for several values of the concentration. The results are shown in Table II. One can see that for PEG 10000 the relative error is below 1%. For all other polymers it is below 2%, except for PEG 300 at $c=0.33$, where it is 2.32%.

The idea to approximate the data on $\eta_{\mathrm{micro}}/\eta_0$ by the formula in Eq. (3.1) came from recent studies of self-diffusion of water in solutions of different substances (sucrose, dextran 40000, PEG 2000, 6000, 20000, and 40000).[33,34] Self-diffusion coefficients were determined by
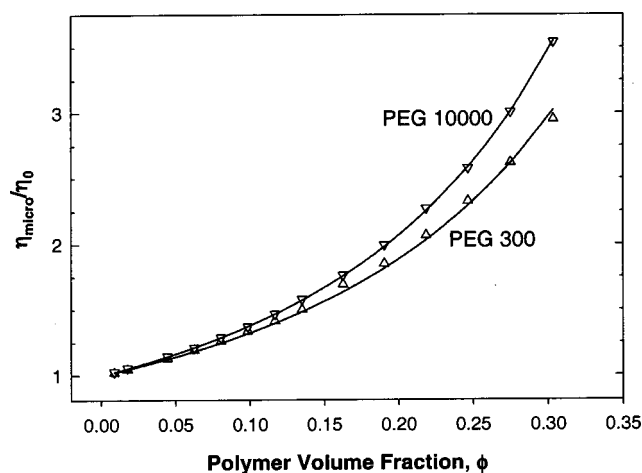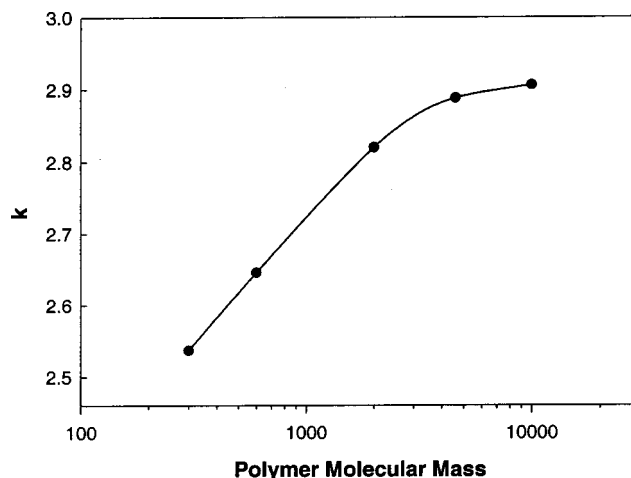


FIG. 6. Dependence of the fitting parameter $k$ on the polymer molecular mass.

pulsed field gradient NMR. It was found that their dependence on the composition of the solutions was well described by the relation,

$$\frac{D}{D_0} = \exp\left( -\kappa\,\frac{N_m}{N_{\mathrm{H_2O}}} \right), \tag{3.3}$$

where $N_m$ and $N_{\mathrm{H_2O}}$ are the numbers of monomeric units of the polymer and water molecules in the solution and $\kappa$ is a fitting parameter. Using the fact that

$$\frac{N_m}{N_{\mathrm{H_2O}}} \propto \frac{\phi}{1-\phi}, \tag{3.4}$$

one can see that relations in Eqs. (3.1) and (3.3) are equivalent.

## IV. DISCUSSION

When analyzing their data on conductivity of PEG containing electrolyte solutions the authors of Refs. 8 and 9 used different versions of the effective medium theory (EMT). This theory treats transport in micrononuniform media by replacing the nonuniform media by a fictitious uniform media with prescribed effective parameters.[23–25] In our case the theory suggests a relation between conductivity of the solution and the volume fraction of nonconducting inclusions, $\phi'$. The latter is assumed to be proportional to the polymer volume fraction, $\phi' = h\phi$. Factor $h$ is greater than unity because nonconducting inclusions contain both the polymer



FIG. 5. Fitting the ratio $\eta_{\mathrm{micro}}/\eta_0$ for PEG 300 and PEG 10000 by the dependence in Eq. (3.1) with $k=2.537$ and $k=2.906$, respectively.

TABLE II. Relative error (in percent) in the conductivity fitting.

| $c$ | 0.05 | 0.09 | 0.15 | 0.24 | 0.33 |
|-----|------|------|------|------|------|
| PEG 300 | −0.44 | −1.17 | −1.11 | −1.75 | 2.32 |
| PEG 600 | −0.90 | −1.10 | −1.65 | −1.23 | 1.80 |
| PEG 2000 | 0.23 | −0.23 | −1.12 | −1.44 | 1.26 |
| PEG 4600 | −0.25 | −0.96 | −1.56 | −1.04 | 1.20 |
| PEG 10000 | −0.27 | −0.04 | −0.46 | −0.85 | 0.26 |

and its hydration water. This factor can be used to estimate the hydration number, which is the number of the hydration water molecules per ethylene oxide group.

In Ref. 8 the authors assumed that nonconducting inclusions are spheres and used the relation,[24]

$$\frac{\sigma}{\sigma_0} = \frac{2(1-\phi')}{2+\phi'}, \qquad (4.1)$$

which follows from the formula derived by Maxwell in Ref. 23. Since this relation is correct only to the first order in $\phi'$, the authors of Ref. 8 also used the relation derived in studies[35,36] in the framework of a more general version of EMT,

$$\frac{\sigma}{\sigma_0} = (1-\phi')^{3/2}. \qquad (4.2)$$

Fitting their data by the dependencies in Eqs. (4.1) and (4.2) the authors of Ref. 8 found that the $h$-factor weakly depended on the polymer molecular mass and decreased from 2.4 to 1.6 as $\phi$ increased from 0.09 to 0.57. It turned out that the two versions of EMT led to close results.

The authors of Ref. 9 used the relation

$$\frac{\sigma}{\sigma_0} = (1-\phi')^3, \qquad (4.3)$$

which had been derived in Ref. 37 in the framework of another version of EMT. Fitting their own data together with the data reported in Ref. 8 they suggested $h=1.2$ for the entire range of the volume fraction $\phi$. This value is smaller than the values obtained in Ref. 8.

Thus, when describing the dependence of the conductivity on the polymer volume fraction in terms of the relations suggested by EMT one has to use the $h$-factor, which is a poorly defined parameter. Indeed, its value depends on which version of EMT is used. Moreover, for some versions $h$-factor varies with the polymer volume fraction. As a consequence, the hydration numbers obtained using different EMT-expressions for the conductivity differ from each other. They also differ from hydration numbers deduced from the measurements of other properties of the solution.

It is interesting to compare limiting behavior of the conductivity predicted by different formulas when $\phi \to 0$. Expressions in Eqs. (4.1) and (4.2) with $h=2.4$ lead to

$$\frac{\sigma}{\sigma_0} \cong 1 - \frac{3}{2}h\phi = 1 - 3.6\phi. \qquad (4.4)$$

Expressions in Eq. (4.3) with $h=1.2$ lead to

$$\frac{\sigma}{\sigma_0} \cong 1 - 3h\phi = 1 - 3.6\phi. \qquad (4.5)$$

Our approximate formula written in terms of $\phi$ is

$$\frac{\sigma}{\sigma_0} = (1-\phi)\exp\left(-k\frac{\phi}{1-\phi}\right). \qquad (4.6)$$

In the small-$\phi$ limit it leads to

$$\frac{\sigma}{\sigma_0} \cong [1-(k+1)\phi] \cong \begin{cases} 1 - 3.5\phi & \text{for PEG } 300 \\ 1 - 3.9\phi & \text{for PEG } 10000. \end{cases}$$
$$(4.7)$$

One can see that all the formulas predict similar behavior of the conductivity at small $\phi$. Small variation in the factor $(k+1)$ in Eq. (4.7) could be related to small variation of the intrinsic conductivity of the inclusion-containing solution due to the difference in the shape of the inclusions. Intrinsic conductivity defined as a limiting value of the ratio $(\sigma-\sigma_0)/(\sigma_0\phi)$ when $\phi \to 0$, varies from 3/2 for spherical inclusions to 5/3 for needlelike inclusions.[38]

In summary, the main result of this study is the expression in Eq. (3.2), which perfectly describes conductivity of PEG containing electrolyte solutions as a function of the PEG concentration for the entire range of the concentration. We arrived at this expression by analyzing the dependence of microviscosity on the polymer volume fraction. Microviscosity introduced by the relation in Eq. (1.2) describes the decrease in the ion mobility due to their collisions with the obstacles rather than changes in the mechanism of dissipation.

[1] O. V. Krasilnikov, R. Z. Sabirov, V. I. Ternovsky, P. G. Merzliak, and J. N. Muratkhodjaev, FEMS Microbiol. Immunol. **105**, 93 (1992).
[2] S. M. Bezrukov and I. Vodyanoy, Biophys. J. **64**, 16 (1993).
[3] S. M. Bezrukov, I. Vodyanoy, and V. A. Parsegian, Nature (London) **370**, 279 (1994).
[4] S. M. Bezrukov, I. Vodyanoy, R. A. Brutyan, and J. J. Kasianowicz, Macromolecules **29**, 8517 (1996).
[5] O. V. Krasilnikov, J. B. Da Cruz, L. N. Yuldasheva, W. A. Varanga, and R. A. Nogueira, J. Membr. Biol. **161**, 83 (1998).
[6] P. G. Merzlyak, L. N. Yuldasheva, C. G. Rodrigues, C. M. M. Carneiro, O. V. Krasilnikov, and S. M. Bezrukov, Biophys. J. **77**, 3023 (1999).
[7] T. K. Rostovtseva, E. M. Nestorovich, and S. M. Bezrukov, Biophys. J. **82**, 160 (2002).
[8] K. R. Foster, E. Cheever, and J. B. Leonard, Biophys. J. **45**, 975 (1984).
[9] F. Bordi, C. Cametti, and A. Di Biasio, J. Phys. Chem. **92**, 4772 (1988).
[10] Y. Marcus, *Ion Properties* (Dekker, New York, 1997).
[11] R. A. Robinson and R. H. Stokes, *Electrolyte Solutions* (Butterworths, London, 1965).
[12] M. Doi and S. F. Edwards, *The Theory of Polymer Dynamics* (Clarendon, Oxford, 1986).
[13] S. G. J. M. Kluijtmans, G. H. Koenderink, and A. P. Philipse, Phys. Rev. E **61**, 626 (2000).
[14] K. A. Streletzky and G. D. J. Phillies, J. Phys. Chem. B **103**, 1811 (1999).
[15] X. Ye, P. Tong, and L. J. Fetters, Macromolecules **31**, 5785 (1998).
[16] D. Langevin and F. Rondelez, Polymer **19**, 875 (1978).
[17] G. D. J. Phillies, J. Phys. Chem. **93**, 5029 (1989).
[18] G. D. J. Phillies, J. Phys. Chem. **96**, 10 061 (1992).
[19] A. G. Ogston, B. N. Preston, and J. D. Wells, Proc. R. Soc. London, Ser. A **333**, 297 (1973).
[20] A. R. Altenberger and M. Tirrell, J. Chem. Phys. **80**, 2208 (1984).
[21] A. R. Altenberger, M. Tirrell, and J. S. Dahler, J. Chem. Phys. **84**, 5122 (1986).
[22] R. I. Cukier, Macromolecules **17**, 252 (1984).
[23] J. C. Maxwell, *A Treatise on Electricity and Magnetism* (Oxford University Press, Oxford, 1873).
[24] H. Fricke, Phys. Rev. **24**, 575 (1924).
[25] T. C. Choy, *Effective Medium Theory, Principles and Applications* (Clarendon, Oxford, 1999).

[26] J. M. Stokes and R. H. Stokes, J. Phys. Chem. **60**, 217 (1956).

[27] T. G. Hiss and E. L. Cussler, AIChE J. **19**, 698 (1973).

[28] K. T. Yam, D. K. Anderson, and R. E. Buxbaum, Science **241**, 330 (1988).

[29] G. Barstein, A. Almagor, S. Yedgar, and B. Gavish, Phys. Rev. E **52**, 555 (1995).

[30] W. H. Green, J. Chem. Soc. **93**, 2049 (1908).

[31] G. L. Pollack and J. J. Enyeart, Phys. Rev. A **31**, 980 (1985).

[32] G. L. Pollack, R. P. Kennan, J. F. Himm, and D. R. Stump, J. Chem. Phys. **92**, 625 (1990).

[33] V. A. Sevrjugin and V. D. Skirda, Zh. Fiz. Khim. **73**, 853 (1999) (in Russian).

[34] V. A. Sevrjugin, I. Yu. Aslanjan, and V. D. Skirda, Zh. Fiz. Khim. **74**, 2167 (2000) (in Russian).

[35] T. Hanai, in *Emulsion Science*, edited by P. Sherman (Academic, New York, 1968), pp. 353–478.

[36] D. A. G. Bruggemann, Ann. Phys. (Paris) **24**, 636 (1935).

[37] H. Looyenga, Physica (Amsterdam) **31**, 401 (1965).

[38] J. Douglas and E. Garboczi, Adv. Chem. Phys. **91**, 85 (1995).